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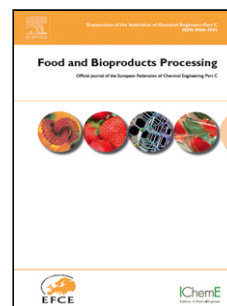
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Integrated Intermediate Catalytic Pyrolysis of Wheat Husk

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Graphical abstract



Highlights:

- Thermo-catalytic reforming of wheat husk in a laboratory scale plant (2 kg/hr).
- Effect of char recycling in reforming stage on gaseous product compositions.
- Bio-oil composition and properties obtained from thermo-catalytic reforming of wheat husk.
- In order to use wheat husk oil as a direct engine fuel, it is necessary to carry out upgrading via hydro-processing; or blend with fossil crude oil for further refining.

ABSTRACT

Lignocellulosic biomass is the most abundant renewable resource in existence and is the only source of renewable fixed carbon. Biofuels produced from this source are promising because they do not

contribute to extra CO₂ emissions and they reduce our dependence on fossil fuels. Presently, wheat husk has a distinctive potential as a renewable source of biomass, due to its global availability, which is advantageous for producing liquid and gaseous fuels by thermochemical processes. The Thermo-Catalytic Reforming (TCR) process is excellent for generating energy vectors (solid char, liquid bio-oil and permanent gases) from agricultural wastes, such as wheat husk. These valorised energy vectors can be applied as transportation fuels and used in combined heat and power (CHP) plants. The aim of this work is to study the conversion of wheat husk into fuels, using TCR technology in a 2 kg/h continuous pilot scale reactor. Findings show that from 100 wt% of the feedstock, 29.6 wt% was converted into synthesis gas, 21.7 wt% to char, 5.8 wt% into organic bio-oil, 32.8 wt% into aqueous phase liquids and the remaining was attributed to losses (10.1 wt%). The organic bio-oil contains a higher heating value (HHV) of 26 MJ/kg, which represents a notable increase compared to the original feedstock (17.8 MJ/kg). Phenol was found to be the most abundant compound within the oil, with a relative abundance of 30.88% measured by GC-MS. Oleic acid (7.41%) was the most abundant long chain hydrocarbon detected. The total acid number of the oil (TAN) was (29.9 mg KOH/g) and viscosity measured (145.2 cSt). In order to use wheat husk oil as a direct engine fuel, it is necessary to carry out upgrading via hydro-processing; or blend with fossil crude oil for further refining. Overall, TCR is a promising future route for the valorisation of wheat husk to produce renewable energy vectors.

Abbreviations: TCR, Thermo-Catalytic Reforming; HHV, higher heating value; CHP, combined heat and power; TCD, thermal conductivity detector; TAN, total acid number; HDO, hydro-deoxygenation; PFD, process flow diagram.

Keywords: Thermo-Catalytic Reforming, pyrolysis, biofuel, wheat husk, biomass

1. INTRODUCTION

Concerns over energy demand and security, together with the impact of CO₂ emissions from fossil fuel usage, contributing towards climate change are driving the need to find alternative and sustainable low carbon energy sources (Jacobson, 2009; Wilson and Lee, 2016). Biofuels are considered as one of the most efficient routes for reducing transportation emissions and dependence on fossil fuels (Shaheen and Lipman, 2007). Among the many possibilities for biofuel production and supply, fuels from biomass are interesting because they do not contribute extra CO₂ emissions and additionally, this option reduces the amount of biogenic wastes and residues entering landfill and incinerators. Lignocellulosic biomass is the most abundant renewable resource existing, the only source of renewable fixed carbon and is considered to be a promising feedstock for the production of sustainable fuels for the future (Lichtenthaler and Peters, 2004; Liu et al., 2014; Maurya et al., 2015).

From all available types of lignocellulosic biomass, wheat husk arising from cereal and food production has become popular. Approximately 1.5 tons of wheat husk is produced per each ton of cereal. In other words, if cereal production exceeds 1000 million tons per year, about 1500 million tons of waste will be generated for the same period (Yuan and Sun, 2010). These agricultural residues have no further value and they are mainly burned to produce energy or used as animal feed. The large availability of these waste resources and also their local accessibility emphasises the potential for them to be used in thermal conversion processes for energy production. Wheat husk is a lignocellulosic residue product (15-20% of wheat is composed of the husk) and its composition is mainly cellulose (36%), hemicellulose (18%) and lignin (16%) (Bledzki et al., 2010; Singh et al., 2013). One of the applications of wheat husk is for cattle food and alcohol production after fermentation (Mohanty et al., 2002). Additionally, it can be the source for specific chemicals and biofuel production.

Production of bio-oil by pyrolysis (Bridgwater, 2012; Torri et al., 2016), hydrothermal liquefaction (Elliott et al., 2015; Toor et al., 2011) or gasification (Yung et al., 2009) and subsequent Fischer–Tropsch synthesis (Jahangiri et al., 2014; Mahmoudi et al., 2017) are the main thermochemical technologies to convert lignocellulosic biomass into liquid biofuels. Pyrolysis is generally characterised into three main groups: slow, intermediate and fast. Each applies different heating rates, temperatures and vapour/solid residence times to the feedstock, but a common parameter is that heating of the feedstock always occurs under starved or oxygen free atmospheres.

Every type of pyrolysis process produces the same products (bio-oil, biochar and syngas), which are highly variable depending on the pyrolysis technique applied (Bridgwater, 2012). Slow pyrolysis involves low heating rates, long residence times and the main product is char. Fast pyrolysis applies high heating rates, short vapour residence times and yields higher quantities of liquids (up to 75 wt% on a dry basis) (Bridgwater, 2012). Intermediate pyrolysis occurs at temperatures between 400 to 500 °C, solid heating rates (minutes), solid residence times (minutes), with a short vapour residence time (seconds) (Neumann et al., 2016b) and produces relatively equal yields of all products, solids, liquids and gases. Depending on the feedstock and process parameters applied, intermediate pyrolysis can yield energy vectors with improved physical and chemical properties (Neumann et al., 2016b). Valorised properties often include high calorific values, lower oxygen content oils and better oil miscibility with fossil fuels, which makes their application in existing engines attractive.

The Pyroformer® (Hornung et al., 2011) intermediate pyrolysis reactor was one of the first intermediate pyrolysis reactors to be built and is essentially an auger screw reactor comprising of two co-axial rotating screws. During the process, the inner and outer screws work together to transport a combination of fresh biomass and recycled char product through the reactor (Yang et al., 2014). The effect of char recycling is the novelty of this reactor type, believed to have the effect of an additional catalytic function in the process, leading to pyrolysis oils with improved fuel characteristics when compared to bio-oils produced from other processes. The formation of de-oxygenated bio-oil with a low molecular weight, low water content and low in tar composition has been observed by the process (Yang et al., 2013).

The development of intermediate pyrolysis later evolved into the Thermo-Catalytic Reforming (TCR®) process. TCR is a new technology which is a combination of intermediate pyrolysis and post catalytic treatment (reforming). This process contains two essential steps: 1) intermediate pyrolysis where the thermal heating of biomass occurs under the complete absence of oxygen, at intermediate heating rates (minutes) and solid residence times (minutes); and 2) the reforming stage where the catalytic cracking of vapours occurs at elevated temperatures to promote the formation of synthesis gas and organic vapours, which when condensed, yield de-oxygenated bio-oils with superior physical and chemical fuel properties (Ejaz et al., 2018; Jäger et al., 2016; Kirby et al., 2017; Neumann et al., 2015).

Within the reformer of TCR, organic vapours are catalytically reformed into higher yields of synthesis gas at temperatures >600 °C. The gases exiting the reactor are fully condensed, generating three different products: an organic bio-oil (6-11 wt%), and aqueous phase liquids (21-26 wt%) and permanent gas fraction (27-44 wt%). The main composition of the permanent gases formed are hydrogen (20-55 vol %), carbon dioxide (15-35 vol%) and carbon monoxide (20-30 vol%) some light hydrocarbon formation is also observed (5-15 vol%).

The overall aim of this work was to study the feasibility of wheat husk conversion into fuels, using TCR technology in a continuous pilot scale reactor; and furthermore, to compare the properties of the oil produced with biodiesel for potential engine applications.

2. MATERIALS AND METHODS

2.1 Raw Material

Wheat husk used in the TCR experiment was supplied from Rosenmuhle GmbH, Germany and it was received with a moisture content <15 wt%; therefore, no drying was required before the thermal conversion. Pelletisation was necessary and performed using a KKP 300 F (22 kWe) motorised pelletiser with total capacity of 300 kg/h throughput (pellets formed were 6 mm diameter by 20 mm length). Prior to pelletising, the feedstock was analysed in order to determine the proximate, ultimate compositions and higher heating value (HHV).

2.2 Experimental Set-up

The TCR-2 bench scale reactor was constructed, installed and commissioned at the laboratory of Fraunhofer UMSICHT Institute, Germany with a capacity to process up to 2 kg/h of biomass. The system was comprised of a sealed hopper with capacity to hold a maximum of 5 kg of material, the main TCR reactor, a condensing unit, filtration system and a gas totaliser and analyser. The process flow diagram (PFD) of the experimental setup is shown in Fig. 1.

The two reactors (auger screw and post reformer) were connected in series. The first intermediate pyrolysis (350-450 °C, heating rate 1 °C/s) reactor with a length of 1000 mm conveys feedstock by means of an auger (ID of screw 80 mm). The auger conveys pyrolysis material into a second stage post-reformer (heated to 600 °C) via electrical ceramic heating elements. The whole system operated in the complete absence of oxygen using a nitrogen purge. Pyrolysis vapours were cracked catalytically (reaction between pyrolysis gases and char) into condensable organic vapours and synthesis gas rich in hydrogen. Condensable vapours were quenched by means of a shell and tube condenser (cooling water, glycol mixture cooled to -5 °C) within a u-tube condenser. Condensable vapours exiting the condenser were further quenched by means of an ice bath cooler. The remaining vapours were directed into two-gas wash bottles, one filled with biodiesel and the other filled with water for aerosol capture. Then the permanent gases were directed to an online gas analyser/calorimeter for detection and gas totalisation before flaring.

At the beginning of the experiment, the auger reactor and post reformer were gradually heated to and average temperature of 430 °C and 600 °C respectively for 80 minutes before the introduction of feedstock. During the heating process the rotating screws were also turned on and the speeds of the inner and outer screws were 4 rpm and 1.25 rpm respectively. Once the TCR had reached steady state temperature it was fed with pelletised feedstock at a rate of up to 1.4 kg/h, with a total of 3 kg of biomass fed throughout the whole experiment. The solid residence time was estimated to be between 5 and 10 minutes. The experiments were performed with a slight TCR over pressure of 100 mbar.

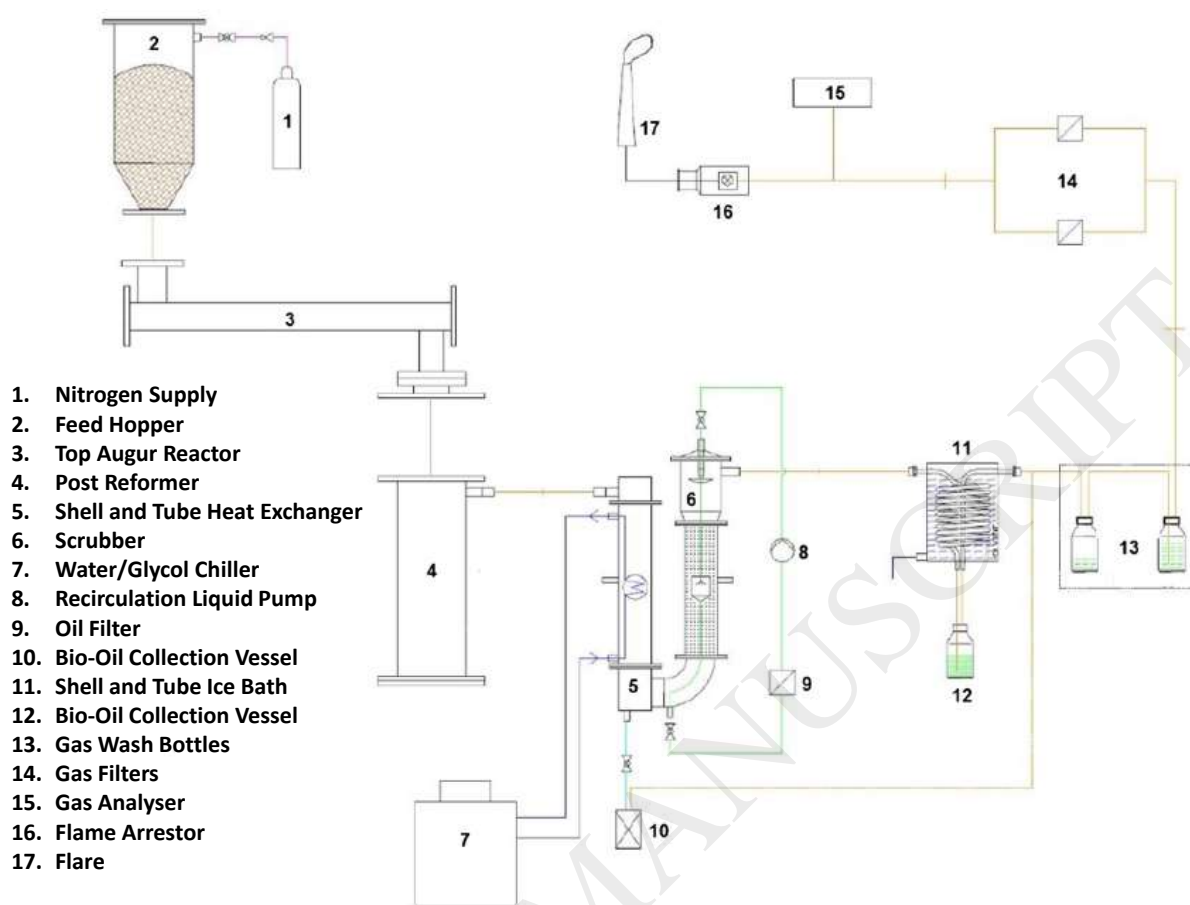


Fig. 1. Process path flow diagram (PFD) of the TCR (2 kg/h) plant

2.3 Proximate Analysis

Moisture content was measured at 105 ± 3 °C in a muffle furnace (Philips K5 94) with an air atmosphere until constant mass was achieved and the percentage moisture was calculated from the loss in mass of the sample (according to ASTM E1756-08). The ash content was measured using the same muffle furnace at 575 ± 25 °C, in which the ash content was determined by the calculation from the mass of the residue remaining after the sample was heated in air under rigidly controlled conditions of time (according to ASTM E1755-01). Volatiles and fixed carbon were determined by thermo-gravimetric analysis (TGA). Approximately 15 mg of dried feedstock was inserted into a crucible and pyrolysed under an inert atmosphere of nitrogen at a flow rate of 60 ml/min, to a maximum temperature of 900 ± 10 °C, with a heating rate of 10 °C/min and holding time of 15 minutes (according to BS EN 15148:2009).

2.4 Ultimate Analysis

Prepared samples were sent to an external laboratory (MEDAC Ltd) for CHNS analysis (with oxygen determined by difference). The C, H, N analysis was carried out according to ASTM E777 and ASTM

E778. The sulphur content was measured according to ASTM E775. The original analytical method (using the Thermo FlashEA® 1112 Elemental Analyser) was based on the complete and instantaneous oxidation of the sample by “flash combustion” which converts all organic and inorganic substances into combustion products. The resulting combustion gases passed through a reduction furnace and were swept into the chromatographic column by the carrier gas (He); where they were separated and detected by a thermal conductivity detector (TCD), which gave an output signal proportional to the concentration of the individual components of the mixture.

2.5 Higher Heating Value (HHV)

The HHV (MJ/kg) was determined using the unified correlation for fuels developed by Channiwala et al. (Channiwala and Parikh, 2002) where C, H, S, O, N and A are carbon weight fraction, hydrogen, sulphur, oxygen, nitrogen and ash, respectively see (eq 1):

$$(eq\ 1). \quad HHV\ (MJ/kg) = 0.3491\ (C) + 1.1783\ (H) + 0.1005\ (S) - 0.1034\ (O) - 0.0151\ (N) - 0.0211\ (A)$$

2.6 Products Characterisation

After the experiment, the produced liquid was separated by gravity (using a separating funnel) into two phases with different densities: an organic oil phase at the top and an aqueous phase at the bottom. Then, the pyrolysis-oil was analysed to determine the chemical and physical properties.

2.6.1 Oil Ultimate Analysis

Pyrolysis liquid and char samples needed to be analysed externally at MEDAC Ltd, applying the same method as in section 2.4 for the determination of the elemental compositions (C, H, N, O and S). Furthermore, the oxygen was determined by the difference by (eq 2).

$$(eq\ 2). \quad 100 - \sum CHNS + ash.$$

2.6.2 Oil Ash Content

The ash content of the oil was calculated in accordance with ASTM D482. The carbonaceous solid samples produced from the carbon residue test were combusted in a muffle furnace at 775 °C. The remaining ash was cooled at room temperature and weighed, then expressed as a mass percentage of the original oil sample. The ash of the char was determined in a muffle furnace at 575 °C, described in section 2.3 according to ASTM E1755-01.

2.6.3 HHV

The HHV of the bio-oil and char was determined using the unified correlation for fuels as described in section 2.5.

2.6.4 Water Content

The water content of the bio-oils was determined using a Mettler Toledo V30 compact volumetric Karl Fischer titration in accordance with ASTM E203-01. The result was corrected to weight percent of the total sample.

2.6.5 Total Acid Number (TAN) and Kinetic Viscosity

The TAN of the oils was determined with a Mettler Toledo V20 compact titrator using the potentiometric titration method in accordance with ASTM D664. The oil sample was dissolved in a 50/50 toluene and isopropanol solution and titrated potentiometrically with 0.1 N alcoholic potassium hydroxide using a combination electrode. Readings were automatically plotted against the volume of the titrating KOH solution used until the titration end-point was achieved. Furthermore, the kinetic viscosity of the bio-oil was determined in accordance with ASTM D445-06.

2.6.6 Gas Chromatography Mass Spectrometry (liquid-GC-MS)

The bio-oil sample was analysed with GC-MS apparatus equipped with a polar chromatographic column. The polar analysis was performed with a 7820A Agilent HP gas chromatograph connected to a 5977E Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan/s within the 29-300 m/z range). Analytes were separated by a nitroterephthalic-acid-modified polyethylene glycol DB-FFAP (30 m, 0.25 mm i.d., 0.2 μ m film thickness) column using helium as a carrier gas with the following thermal program: 50 °C with a hold for 5 minutes; then ramping up with a heating rate of 10 °C/min until 250 °C; followed by column cleaning at 250 °C for 10 minutes. A sample of bio-oil was dissolved in acetonitrile solution to a 1% (w/v concentration), spiked with 0.1 ml internal standard solution (1000 mg/l, 2-ethyl butyric acid in acetonitrile). The compounds were identified by library searches (NIST libraries) and mass spectra evaluation and, were quantified in terms of relative abundance of peak area (% peak area to the total area).

2.6.7 Gas Analysis

The produced pyrolysis gas was frequently measured and analysed using a gas analyser MGA 12, Dr. Födisch Umweltmesstechnik according to EN 15267-3 standard test procedure. The measurement principle of the gas analyser is based on an infrared photometer (CO, CO₂ and CH₄), an electro chemical cell (O₂) and a TCD (H₂). The heating value of the gas phase was quantified using the Union Instruments CWD2005 process gas analyser. The calibration of the gas analysers was performed prior to the experiments.

3. RESULTS AND DISCUSSION

3.1 Wheat Husk

The proximate and ultimate analysis (determined on a moisture free basis) of the wheat husk pellets used in the TCR experiments are shown in Table 1. The carbon, hydrogen, nitrogen and moisture contents (42, 6.3, 1.9 and 7 wt% respectively) of the wheat husk pellets are similar to the results obtained by Krishna et al. (Krishna et al., 2015) (38.5, 5.2, 1.0 and 7.7 wt% for C, H, N and moisture, respectively) for the same type of biomass. However, the same study showed a higher level of ash (13.9 wt.%), which reduces the calorific value of the char (Mayer et al., 2012).

Table 1. Feedstock characterisation

	Unit	Value
Ultimate analysis (moisture free basis)		
C	wt%	42.0
H	wt%	6.3

N	wt%	1.9
S	wt%	<0.1
O (difference)	wt%	47.4
Proximate analysis (dry basis)		
Moisture	wt%	7.0
Ash	wt%	2.3
Fixed carbon	wt%	19.3
Volatiles	wt%	71.4
HHV	MJ/kg	17.8

3.2 Bio-oil Analysis

The properties of the bio-oil organic phase, after separation from the aqueous phase, are shown in Table 2. The results show an increase in C (56.3 wt%) and H (7.8 wt%), low O (29.7 wt%) content and subsequently a notable increase of the HHV (26 MJ/Kg) when compared to the original feedstock. The low oxygen content of bio-oils makes them suitable fuels because this increases the heating value of the oil and makes the oil less prone to aging effects and polymerisation over time (Ouadi et al., 2018). Comparing these values with the original feedstock, the potential of the TCR technology in valorising the energy density of biofuels per unit volume is clearly recognised. Yang et al. (Yang et al., 2014) and Mahmood et al. (Mahmood et al., 2013) worked with intermediate pyrolysis using wood pellets and brewers spent grain as a feedstock, respectively. The HHVs presented were lower (24.2 and 20.39 MJ/kg, respectively) in comparison to the present study (26 MJ/kg), which can be explained as being due to the catalytic activity occurring inside the post-reformer (Neumann et al., 2016a). However, the HHV of diesel is 45.36 MJ/kg, about double the energy content of this bio-oil. The difference between bio-oil and diesel is related to the higher oxygen content of biomass-derived fuels, due to the presence of certain compounds such as carboxyl hydroxyl, aldehyde, ether and carbolic groups (Liu et al., 2014).

Water produced in the process is formed as a result of residual moisture within the biomass and also moisture formed during dehydration reactions in the pyrolysis process. The presence of a small amount of water within the oil has the effect of reducing combustion temperatures and subsequently reducing NO_x emissions in engines (Ouadi et al., 2013). Some moisture present in the oil also has the effect of decreasing viscosity and promoting atomisation of the bio-oil (Ikura et al., 2003). The TAN of the wheat husk oil (29.9 mg KOH/g) is considered lower than that of the wood oil from the study of Yang et al. (Yang et al., 2014) (47.5 mg KOH/g) and of the brewers spent grain oil in the work of Mahmood et al. (Mahmood et al., 2013) (49.2 mg KOH/g); thus indicating a presence of less organic acid compounds within the oil which would lead to a reduction of wear and corrosion in engine component parts. Compared to biodiesel (0.8 mg KOH/g), the acid number found in this work is relatively high for engine applications. In relation to viscosity, the present study indicates a high value due to a lower reforming temperature (600 °C), which would be detrimental to the flow characteristics and, consequently resulting in incomplete combustion and engine power loss if applied in engines. The ash content was <0.001%. This value is acceptable in comparison with diesel (0.01%) and biodiesel (0.10%). To use wheat husk oil, as biofuel, in engines would require further upgrading via hydro-processing or blending in lower ratios with fossil fuels before its use.

Table 2. Bio-oil characterisation

	Unit	Value
Ultimate analysis		
C	wt%	56.3
H	wt%	7.8
N	wt%	4.8

S	wt%	1.4
O (difference)	wt%	29.7
Fuel properties		
Moisture	wt%	<1.0
Ash	wt%	<0.001
TAN	mg KOH/g	29.9
Viscosity	cSt	145.2
HHV	MJ/kg	26.0

3.3 GC-MS Analysis of Bio-oil

The organic fraction of wheat husk bio-oil was analysed through GC-MS. The bio-oil chromatogram can be seen in Fig. 2; while Table 3 lists detected and identified chemicals and their relative abundance. Phenols are the most abundant compound (30.88%), followed by aromatic compounds (18.41%). Benzene (9.63%) was the most abundant aromatic compound followed by naphthalene (3.94%), styrene (2.38%) and p-xylene (1.22%). Furans have a small fraction with 6.88%. The oleic acid (7.41%) was the most abundant long chain hydrocarbon detected.

The formation of these compounds can be explained due to the presence of lignin and other biopolymer components in the biomass, which provide a high level of polymerised aromatics (Yang et al., 2014). Phenols, cyclopenten and furans are all flammable organics. Additionally, aromatic hydrocarbons may guarantee a good combustibility of the oil for application as an energy fuel although fuels with higher aromatic contents do not burn as clean in engines; but their presence within the oil improves blending capabilities with fossil fuels (Ouadi et al., 2017). The higher acidity of the bio-oil produced can be attributed to the large amount of phenol compounds (Mahmood et al., 2013).

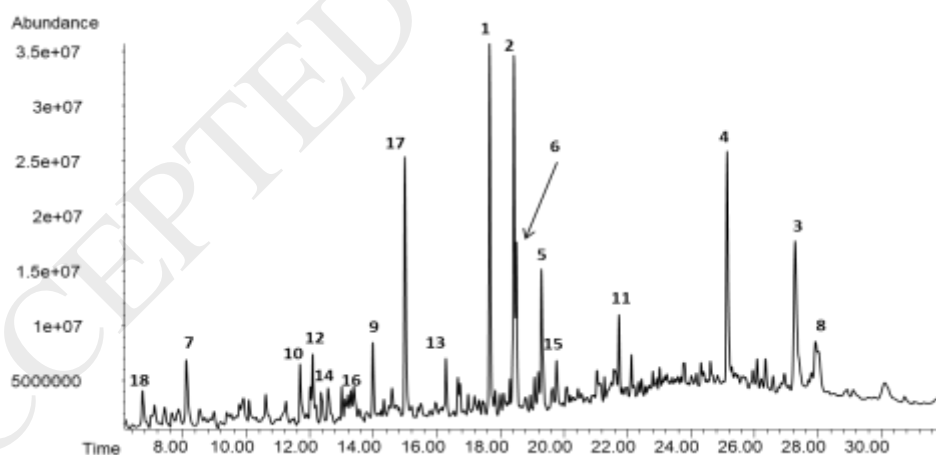


Fig. 2. GC-MS chromatogram of the TCR bio-oil and main compound detected

Table 3. GC-MS (polar column) of the wheat husk bio-oil (organic phase)

#	Compound	Retention time (min)	Area (%)
1	Phenol	17,671	8.94
2	Phenol, 4-methyl	18,441	7.58
3	Oleic acid	27,297	7.41
4	Palmitic acid	25,154	6.59
5	Phenol, 2-ethyl	19,310	3.52

6	Phenol, 3-methyl	18,516	3.48
7	Styrene	8,110	2.38
8	Phenol, 3-methyl	27,938	1.93
9	Furfuryl alcohol	13,987	1.86
10	Benzene, 1-ethynyl-4-methyl	11,694	1.78
11	Indole	21,750	1.73
12	Acetylfuran	12,090	1.64
13	Naphthalene, 1-methyl	16,291	1.49
14	2-Cyclopenten-1-one, 2,3-dimethyl	12,579	1.36
15	Phenol, 2,4-dimethyl	19,782	1.27
16	1H-Indene, 3-methyl	13,392	1.25
17	n.i.	28,043	1.23
18	p-Xylene	6,731	1.22
19	Furan, 2,3,5-trimethyl	11,251	1.11
20	2-Cyclopenten-1-one, 3-methyl	12,359	1.02
21	Benzene, 1-ethenyl-2-methyl-	9,913	0.98
22	1,4-Benzenediol	26,366	0.95
23	Pentanenitrile, 4-methyl	7,868	0.89
24	Phenol, 2-ethyl-5-methyl	19,211	0.89
25	Naphthalene, 1,2-dihydro-6-methyl	14,594	0.88
26	Benzene, 2-propenyl	10,614	0.85
27	1H-Indole, 7-methyl	22,141	0.85
28	n.i.	21,052	0.85
29	n.i.	24,630	0.83
30	1,4-Benzenediol, 2-methyl	26,102	0.83
31	1H-Indene, 3-methyl	13,299	0.82
32	Naphthalene, 1-methyl	16,670	0.82
33	Benzofuran	12,015	0.80
34	Benzofuran, 2-methyl	13,207	0.77
35	n.i.	21,598	0.77
36	1H-Indene, 3-methyl	13,011	0.75
37	Naphthalene, 2-ethyl	17,195	0.75
38	Benzene, 1,2,3-trimethyl-	8,532	0.72
39	Benzene, propyl	7,110	0.71
40	Furan, 3-phenyl	25,964	0.70
41	Phenol, 2,3,5-trimethyl	18,120	0.70
42	n.i.	26,965	0.69
43	Phenol, 2,6-dimethyl	19,087	0.66
44	Phenol, 2,3-dimethyl	16,740	0.65
45	Benzene, 1,3,5-trimethyl	7,431	0.64
46	n.i.	27,812	0.64
47	Phenol, 2-ethyl-4-methyl	19,655	0.63
48	Phenol, 2-ethyl	18,314	0.63
49	Benzaldehyde, 4-ethyl	21,152	0.60
50	n.i.	20,103	0.60
51	1,2-Cyclopentanedione, 3-methyl	15,961	0.59

n.i. (not identified)

3.4 Gas Analysis

The gases detected from the permanent gas fraction (Table 4) were H_2 , CH_4 , CO , CO_2 and C_xH_y ; H_2O was not present, because most of the water was condensed in the cooling system to produce pyrolysis oil. There is no oxidation-reduction reaction during this process due to the total absence of oxygen; and the non-detectable gas fraction (11.4 vol%) can be the presence of hydrocarbons as propane and ethylene.

Biomass decomposition and volatilisation are responsible for the formation of the permanent gases (Sikarwar et al., 2017). CO_2 production is associated with decomposition of hemicellulose and cellulose during the pyrolysis process. This reaction is determined by the amount of oxygen and carbon in the feedstock and degree of carbon vapour mixing within the reactor (Ouadi et al., 2013). CO is formed mainly as a result of Boudouard reactions between carbon and CO_2 and the production of CH_4 is a result of methanation reactions between H_2 and carbon (Yang et al., 2007). The production of CO_2 and H_2 can also be explained by water gas shift reactions and steam methane reforming reactions occurring within the post reformer

The HHV of the permanent gases produced in the present study (20.6 MJ/m^3) is relatively superior to that of Neumann et al. (Neumann et al., 2016b) (14.4 MJ/m^3) which used digestate as a feedstock in the TCR process; and also when compared with the typical gasification syngas ($4\text{--}10 \text{ MJ/m}^3$) (Ruiz et al., 2013). The main reason for this is the higher level of hydrogen present in this gas produced mainly by water gas shift reactions occurring in the post reformer.

Table 4. Gas composition

Component	Unit	Value
H_2	vol%	19.4
CH_4	vol%	12.3
CO	vol%	26.4
CO_2	vol%	26.9
C_xH_y	vol%	3.6
Non-detectable	vol%	11.4
HHV	MJ/m^3	20.6

3.5 Char Analysis

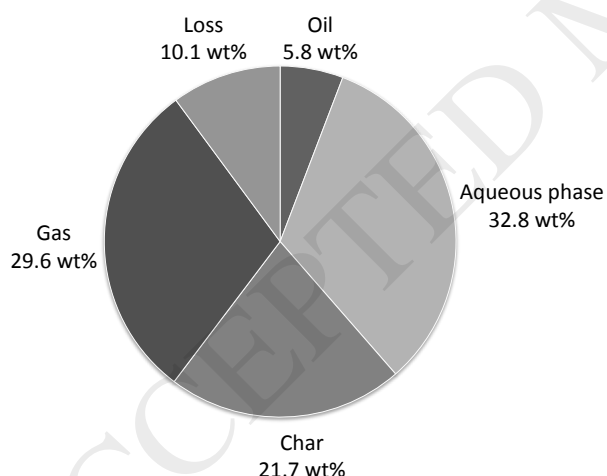
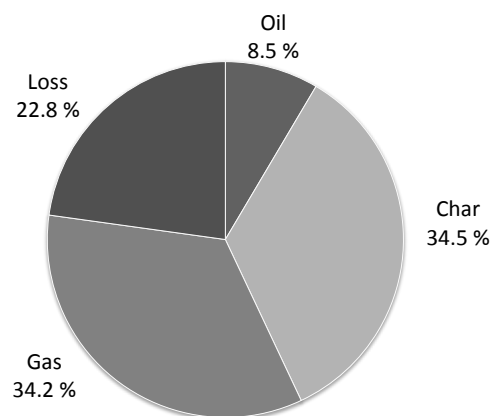
The elemental composition of the char and its energy content is represented in Table 5. It demonstrates that wheat husk char has 76.5 wt% carbon and contains an HHV of 28.4 MJ/kg (approximately 37.3% higher than the original feedstock). The char obtained by Neumann et al. (Neumann et al., 2016b) at the same pyrolysis temperature but with a different reforming temperature (750°C) had a lower HHV (23.9 MJ/kg); however, the feedstock used was digestate (higher ash content). Comparatively with classic subbituminous coal, which has around 73.9% of carbon and contains a HHV of 29.05 MJ/kg (Kabe et al., 2004), this study presented similar results. The extended residence time caused the secondary cracking reaction producing coke and consequently more carbon in the pyrolysis char. The char content is influenced by the reforming temperature used in the TCR and its valuable HHV can be useful for combustion in furnaces, gasifiers and boilers (Mahmood et al., 2013). The same char has other promising applications, such as soil amendment, carbon sequestration and fertiliser (Ouadi et al., 2013).

Table 5. Char characterisation

	Unit	Value
C	wt%	76.5
H	wt%	2.2
N	wt%	3.3
S	wt%	0.1
O (difference)	wt%	6.1
Ash	wt%	11.8
HHV	MJ/kg	28.4

3.6 Mass Balance and Energy Yield

Fig. 3 and 4 indicate the mass balance and energy yields, respectively, for the pelletised wheat husk and the products obtained during the experiment of the TCR. From 100% of the feedstock, 29.6% was converted into pyrolysis gas, 21.7% to char and 5.8% into organic bio-oil. The aqueous phase was the largest produced with 32.8% and the losses represented 10.1%. In the energy yield, approximately 70% of the total energy from the feedstock was converted into the chemical energy of the products, distributed between the char (34.5%) and the permanent gases (34.2%); only 8.5% is attributed to the oil. The system energy losses (including the aqueous phase) represent 22.8% of the energy converted from the original feedstock. The energy losses can be reduced with a better and efficient isolation, and also by increasing the scale of the reactor.

**Fig. 3.** Mass balance**Fig. 4.** Energy yield

4. CONCLUSIONS

Wheat husk was successfully processed using TCR technology in a 2 kg/h continuous pilot scale reactor. The pyrolysis oil, char and gas fraction were effectively produced and characterised. The amount of organic oil, aqueous phase liquid, char and permanent gas produced were 5.8, 32.8, 21.7 and 29.6 wt%, respectively and the remainder was attributed to losses. The energy losses represented 22.8% of the total energy yield and these can be minimised by applying an efficient isolation and

increasing the reactor scale. Phenol was found to be the most abundant compound within the oil, with a relative abundance of 30.88%. Furthermore, oleic acid (7.41%) was the most abundant long chain hydrocarbon detected. The pyrolysis oil has a low HHV (26 MJ/Kg) due to its superior amount of oxygen and water, a high viscosity content (145.2 cSt) and TAN (29.9 mg KOH/g) compared to biodiesel. For that reason, the wheat husk oil, would require further upgrading before applications in engines. Generally, the thermal chemical properties of the bio-oil produced are well suited for blending with fossil fuels. The higher heating value of the char and gas was 28.4 MJ/Kg and 20.6 MJ/m³ respectively. The volumetric percentage of hydrogen was 19.4 vol% and its production could be further optimised by adjusting the reforming conditions, so the process is valuable for hydrogen production. Overall, TCR was shown to be a promising future route for the valorisation of wheat husk (lignocellulosic biomass) in order to produce energy vectors.

REFERENCES

- Bledzki, A.K., Mamun, A.A., Volk, J., 2010. Physical, chemical and surface properties of wheat husk, rye husk and soft wood and their polypropylene composites. *Composites Part a-Applied Science and Manufacturing* 41, 480-488.
- Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 38, 68-94.

- Channiwala, S.A., Parikh, P.P., 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81, 1051-1063.
- Ejaz, A., Jäger, A., Apfelbacher, A., Daschner, R., Hornung, A., Pant, 2018. Integrated thermo-catalytic reforming of residual sugarcane bagasse in a laboratory scale reactor.
- Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., Jones, S.B., 2015. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresource Technology* 178, 147-156.
- Hornung, A., Apfelbacher, A., Sagi, S., 2011. Intermediate pyrolysis: A sustainable biomass-to-energy concept-biothermal valorisation of biomass (BtVB) process. *Journal of Scientific and Industrial Research* 70, 664-667.
- Ikura, M., Stanciulescu, M., Hogan, E., 2003. Emulsification of pyrolysis derived bio-oil in diesel fuel. *Biomass and Bioenergy* 24, 221-232.
- Jacobson, M.Z., 2009. Review of solutions to global warming, air pollution, and energy security. *Energy & Environmental Science* 2, 148-173.
- Jäger, N., Conti, R., Neumann, J., Apfelbacher, A., Daschner, R., Binder, S., Hornung, A., 2016. Thermo-Catalytic Reforming of Woody Biomass. *Energy & Fuels* 30, 7923-7929.
- Jahangiri, H., Bennett, J., Mahjoubi, P., Wilson, K., Gu, S., 2014. A review of advanced catalyst development for Fischer-Tropsch synthesis of hydrocarbons from biomass derived syn-gas. *Catalysis Science & Technology* 4, 2210-2229.
- Kabe, T., Ishihara, A., Qian, E.W., Sutrisna, I.P., Kabe, Y., 2004. Coal and coal-related compounds - Structures, reactivity and catalytic reactions. *Coal and Coal-Related Compounds: Structures, Reactivity and Catalytic Reactions* 150, 127-175.
- Kirby, M.E., Hornung, A., Ouadi, M., Theodorou, M.K., 2017. The role of thermo-catalytic reforming for energy recovery from food and drink supply chain wastes. *Energy Procedia* 123, 15-21.
- Krishna, B.B., Singh, R., Bhaskar, T., 2015. Effect of catalyst contact on the pyrolysis of wheat straw and wheat husk. *Fuel* 160, 64-70.
- Lichtenthaler, F.W., Peters, S., 2004. Carbohydrates as green raw materials for the chemical industry. *Comptes Rendus Chimie* 7, 65-90.
- Liu, C., Wang, H., Karim, A.M., Sun, J., Wang, Y., 2014. Catalytic fast pyrolysis of lignocellulosic biomass. *Chemical Society Reviews* 43, 7594-7623.
- Mahmood, A.S.N., Brammer, J.G., Hornung, A., Steele, A., Poulston, S., 2013. The intermediate pyrolysis and catalytic steam reforming of Brewers spent grain. *Journal of Analytical and Applied Pyrolysis* 103, 328-342.
- Mahmoudi, H., Mahmoudi, M., Doustdar, O., Jahangiri, H., Tsolakis, A., Gu, S., LechWyszynski, M., 2017. A review of Fischer Tropsch synthesis process, mechanism, surface chemistry and catalyst formulation. *Biofuels Engineering* 2, 11-31.
- Maurya, D.P., Singla, A., Negi, S., 2015. An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol. *3 Biotech* 5, 597-609.
- Mayer, Z.A., Apfelbacher, A., Hornung, A., 2012. A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char. *Journal of Analytical and Applied Pyrolysis* 96, 196-202.
- Mohanty, A.K., Misra, M., Drzal, L.T., 2002. Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *Journal of Polymers and the Environment* 10, 19-26.
- Neumann, J., Binder, S., Apfelbacher, A., Gasson, J.R., Ramírez García, P., Hornung, A., 2015. Production and characterization of a new quality pyrolysis oil, char and syngas from digestate – Introducing the thermo-catalytic reforming process. *Journal of Analytical and Applied Pyrolysis* 113, 137-142.
- Neumann, J., Jager, N., Apfelbacher, A., Daschner, R., Binder, S., Hornung, A., 2016a. Upgraded biofuel from residue biomass by Thermo-Catalytic Reforming and hydrodeoxygenation. *Biomass & Bioenergy* 89, 91-97.

- Neumann, J., Meyer, J., Ouadi, M., Apfelbacher, A., Binder, S., Hornung, A., 2016b. The conversion of anaerobic digestion waste into biofuels via a novel Thermo-Catalytic Reforming process. *Waste Management* 47, 141-148.
- Ouadi, M., Brammer, J.G., Yang, Y., Hornung, A., Kay, M., 2013. The intermediate pyrolysis of de-inking sludge to produce a sustainable liquid fuel. *Journal of Analytical and Applied Pyrolysis* 102, 24-32.
- Ouadi, M., Greenhalf, C., Jaeger, N., Speranza, L.G., Hornung, A., 2018. Thermo-catalytic reforming of co-form® rejects (waste cleansing wipes). *Journal of Analytical and Applied Pyrolysis*.
- Ouadi, M., Jaeger, N., Greenhalf, C., Santos, J., Conti, R., Hornung, A., 2017. Thermo-Catalytic Reforming of municipal solid waste. *Waste Management* 68, 198-206.
- Ruiz, J.A., Juarez, M.C., Morales, M.P., Munoz, P., Mendivil, M.A., 2013. Biomass gasification for electricity generation: Review of current technology barriers. *Renewable & Sustainable Energy Reviews* 18, 174-183.
- Shaheen, S.A., Lipman, T.E., 2007. Reducing greenhouse emissions and fuel consumption: Sustainable Approaches for Surface Transportation. *IATSS Research* 31, 6-20.
- Sikarwar, V.S., Zhao, M., Fennell, P.S., Shah, N., Anthony, E.J., 2017. Progress in biofuel production from gasification. *Progress in Energy and Combustion Science* 61, 189-248.
- Singh, R., Bhaskar, T., Dora, S., Balagurumurthy, B., 2013. Catalytic hydrothermal upgradation of wheat husk. *Bioresource Technology* 149, 446-451.
- Toor, S.S., Rosendahl, L., Rudolf, A., 2011. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 36, 2328-2342.
- Torri, I.D.V., Paasikallio, V., Faccini, C.S., Huff, R., Caramão, E.B., Sacon, V., Oasmaa, A., Zini, C.A., 2016. Bio-oil production of softwood and hardwood forest industry residues through fast and intermediate pyrolysis and its chromatographic characterization. *Bioresource Technology* 200, 680-690.
- Wilson, K., Lee, A.F., 2016. Catalyst design for biorefining. *Phil. Trans. R. Soc. A* 374, 20150081.
- Yang, H.P., Yan, R., Chen, H.P., Lee, D.H., Zheng, C.G., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86, 1781-1788.
- Yang, Y., Brammer, J.G., Mahmood, A.S.N., Hornung, A., 2014. Intermediate pyrolysis of biomass energy pellets for producing sustainable liquid, gaseous and solid fuels. *Bioresource Technology* 169, 794-799.
- Yang, Y., Brammer, J.G., Ouadi, M., Samanya, J., Hornung, A., Xu, H.M., Li, Y., 2013. Characterisation of waste derived intermediate pyrolysis oils for use as diesel engine fuels. *Fuel* 103, 247-257.
- Yuan, T.Q., Sun, R.C., 2010. Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose Introduction. *Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels: Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose*, 1-7.
- Yung, M.M., Jablonski, W.S., Magrini-Bair, K.A., 2009. Review of Catalytic Conditioning of Biomass-Derived Syngas. *Energy & Fuels* 23, 1874-1887.

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